Molecular Vibrational Energy Relaxation at a Metal Surface: Methyl Thiolate on Ag(111)

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The lifetime of the first excited level of the symmetric C-H stretching mode of CH_3S chemisorbed on a Ag(111) surface was measured by picosecond vibrational spectroscopy. A biexponential decay (~3- and 63-ps lifetimes at 300 K) was observed, with a substantial temperature dependence of the slow component. Both decay processes are assigned to intramolecular vibrational relaxation. The decay rates are 2 orders of magnitude too fast to be explained by electron-hole-pair damping by the metal substrate.

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Despite the fundamental importance of vibrational energy transfer to chemical processes at metal surfaces, there have been no time-domain measurements of vibrational lifetimes for adsorbates on single-crystal surfaces.[1] This Letter reports such measurements for the first excited level of the symmetric C-H stretching mode of methyl thiolate, CH_3S, chemisorbed on a Ag(111) surface. Previous indirect measurements based on linewidth have assigned the vibrational relaxation of this mode in similar adsorbates [CH_3O/Cu(100) and CH_3C/Pt(111)] to electron-hole-pair excitation in the metal.[2] The present results show that the vibrational linewidth is not determined in CH_3S by vibrational energy relaxation. In addition, the relaxation itself is assigned to intramolecular energy transfer. The previous assignments must be reconsidered. The results demonstrate the importance of intramolecular energy transfer for small polyatomic molecules even where electron-hole-pair damping has previously been assigned dominance.

To measure vibrational relaxation times, a resonant infrared pulse populates the first excited state of the symmetric C-H stretching mode at 2918 cm^{-1}. The subsequent population relaxation is monitored by transient sum-frequency-generation (SFG) spectroscopy.[3] In this method, an SFG signal is generated by mixing a visible probe pulse with a vibrationally resonant infrared probe pulse at the surface. The vibrationally resonant SFG signal is proportional to the square of the population difference between the lower and upper levels of the transition probed.[3] Its square root is therefore a measure of the population difference on the vibrational transition. If S_0 is the SFG signal with no pump and $S(\tau_d)$ is the signal at delay τ_d after the pump, $1-[S(\tau_d)]^{1/2}/\sqrt{S_0}$ is then analogous to a transient absorption probe at resonance;[4] this normalized difference of square roots is proportional to the pump-induced change in the population difference, which is dependent on the probe delay. This description assumes the excited-level absorption is shifted by anharmonicity, so that it does not interfere with the ground-state probe. In the present case, the shift of the excited-state absorption of the symmetric C-H stretching mode is 50–100 cm^{-1}, well outside the probe-pulse bandwidth.[5]

Visible pulses with 4-ps duration (5-cm^{-1} bandwidth) and infrared pulses of 3-ps duration (6-cm^{-1} bandwidth) are generated in a picosecond laser system, as previously described.[3] The infrared pulses have an energy of ~10 μJ and are tunable in the 2750–3050-cm^{-1} region. Two-thirds of this energy is used as a resonant pump and one-third is used as the probe infrared.

Three incident optical beams (infrared pump, infrared probe, and visible probe) are focused to a common 150-μm-diam spot on the sample. All incident fields are *p* polarized at the surface. The vibrationally resonant molecular SFG signal (*p* polarized) is monitored by a monochromator–photomultiplier-tube combination. The anisotropy[6] of the nonlinear response from the threefold-symmetric Ag(111) surface is used to minimize interference from nonresonant substrate SFG signal, by adjusting the azimuthal angle of the crystal and the angle of the SFG polarizer to reduce the substrate signal to 1% of the vibrationally resonant molecular signal.

The sample surface is prepared by sputtering (1 kV, 10 μA at both 25 and 625 °C) and annealing (625 °C). The sample is dosed with ~5 L [1 langmuir (L) = 10^{-6} Torr s] of dimethyl disulfide (Aldrich, 99+%) at 25 °C. Immediately after dosing the SFG spectrum shows a resonance near 2918 cm^{-1} with a width of ~25 cm^{-1} and a long tail to higher frequencies. After 7–8 h in UHV at 25 °C the spectrum (Fig. 1) narrows to a width of 13 cm^{-1}, and an ordered $(\sqrt{7}\times\sqrt{7})R10.9°$ LEED pattern appears. A similar pattern has been observed after dosing Ag(111) with S_2 and H_2S,[7] and has been attributed to an overlayer of γ-Ag_2S. This requires, in the present system, that the S–S bond dissociates, and leaves the methyl thiolate (CH_3S) groups bonded in an ordered monolayer on the surface. Adsorption isotherms using both the SFG signal and thermal-desorption spectroscopy (TDS) indicate that doses above 4 L lead to single chemisorbed monolayers of methyl thiolate (CH_3S), consistent with this picture, and with the behavior of H_2S.[7] The dissociation of the S–S bond is confirmed by a second-order line shape in thermal-desorption experiments and by the vertical orientation of the CH_3 group

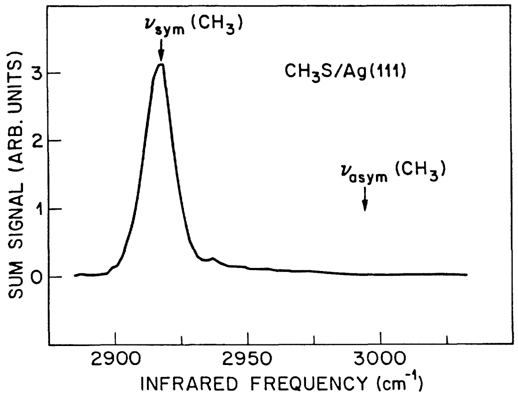

FIG. 1. SFG spectrum in the C-H stretching region of a monolayer of methyl thiolate, CH_3S, on Ag(111) at 25 °C. Mode positions, based on liquid-phase spectra, are marked.

in the SFG spectrum (see below).

The vibrational spectrum in the C-H stretching region (Fig. 1), obtained by SFG spectroscopy, shows only the symmetric C-H stretching mode, and not the asymmetric stretching mode at 2990 cm^{-1}. The asymmetric stretching mode is easily observed in other molecules when its transition dipole is tilted with respect to the surface,[3] and we conclude that the surface dipole selection rule prevents its observation here because its transition dipole is parallel to the surface. The symmetry axis of the CH_3 group, perpendicular to the transition dipole, is therefore perpendicular to the surface.

Figure 2 illustrates the transient signal $1-[S(\tau_d)]^{1/2}/\sqrt{S_0}$, obtained at 25 °C with pump and probe pulses set to the peak of the symmetric C-H stretching mode resonance. The peak change in the SFG signal represents a 40% change of the population difference, or a 20% population of the upper level. The recovery clearly shows two components, a fast (< 5-ps) decay followed by a 63-ps decay. The fast component is barely resolved in the experiment, but it peaks after the pump pulse, at $\tau_d = 4$ ps, and relaxes more slowly than does the cross correlation of the pump infrared pulse with the visible probe. The slow component, on the other hand, is easily resolved, and the variation of the slow decay rate with temperature over the accessible temperature range of the experiment is shown in Fig. 3.

In addition to resonantly exciting the molecule, the infrared pump pulse directly heats the silver surface ~20 °C, based on the optical and heat-diffusion constants of silver. To check for heating effects in the transient spectra, the pump infrared pulse was replaced by a visible pump pulse of the same energy. No SFG transients were observed within the signal-to-noise ratio of the experiment, although 3 to 4 times as much energy is absorbed at the surface from the visible pump pulse. The SFG transient signals, therefore, are directly related to molecular vibrational excitation and decay.

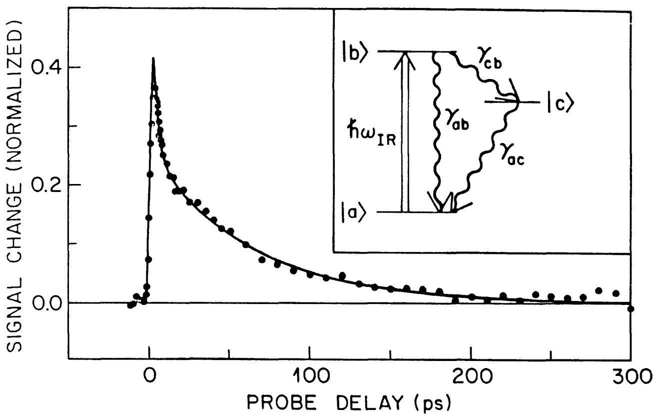

FIG. 2. SFG transient signal at 25 °C with pump and probe at 2918 cm^{-1}. The solid line is calculated using the three-level population decay model shown in the inset, and explained in the text. The level-to-level population decay rates, γ, of the model are labeled in the inset.

We consider the population dynamics in terms of the simple three-level relaxation scheme shown in the inset of Fig. 2, where $|a\rangle$ is the vibrational ground state and $|b\rangle$ is the excitated level. The nature of the third level, $|c\rangle$, is discussed below. The level-to-level population relaxation rates, γ, are also identified in Fig. 2. In the three-level model, with $\gamma_{cb} \gg \gamma_{ab}, \gamma_{ac}$, the transient signal will show a partial (~50%) recovery as level $|b\rangle$ is depopulated, and a slower complete recovery to the equilibrium signal as level $|a\rangle$ is repopulated, in qualitative agreement with the observed dynamics. The time-dependent population difference induced by a δ-function pump pulse is proportional to $F_1(t)$,[4]

$$F_1(t) = \left[\left(2 - \frac{\gamma_{cb}}{\gamma_b - \gamma_{ac}} \right) e^{-\gamma_b t} + \left(\frac{\gamma_{cb}}{\gamma_b - \gamma_{ac}} \right) e^{-\gamma_{ac} t} \right], \quad (1)$$

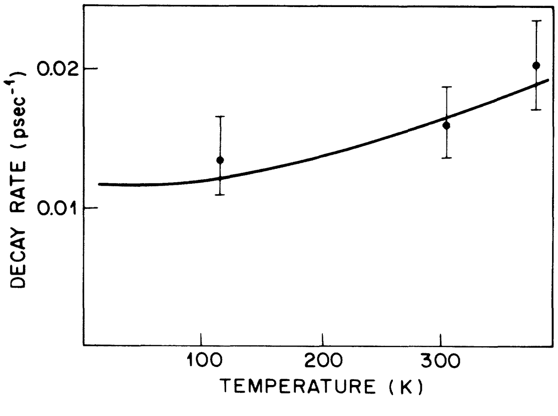

FIG. 3. Temperature dependence of the slow component of the population decay. Error bars are 95%-confidence limits based on multiple data sets. The solid line is a calculation for a perturbation model of relaxation of a 2920-cm^{-1} mode to two modes at 1360 cm^{-1} and one mode at 200 cm^{-1}.

where $\gamma_b = \gamma_{cb} + \gamma_{ab}$ is the total population relaxation rate of the upper level, $|b\rangle$.

The time dependence of the signal is determined by a convolution of the pump and probe pulses with $F_1(t)$. The 25 °C data in Fig. 2 are modeled using Gaussian visible and infrared pulses of 4-ps duration. The population relaxation time $1/\gamma_{ac}$ is set to 63 ps, assumed to account for the slow relaxation component. The population relaxation time $1/\gamma_{cb}$ is varied to find the best fit to the early-time dynamics, while direct relaxation of level $|b\rangle$ to level $|a\rangle$ is assumed to be slow enough to be negligible in comparison with the short relaxation time $1/\gamma_{cb}$. The best value of $1/\gamma_{cb}$ is 3 ps. The full calculation of the transient signal also includes coherent mixing artifacts near zero delay which are, however, found to be small ($\sim$15% of the peak signal at $\tau_d = 4$ ps).[4] The best-fit curve for the three-level model, including coherent effects, is shown as the solid line in Fig. 2.

We note that the linewidth (FWHM) expected from the lifetime broadening alone is $1/2\pi c T_1$, or 1.8 cm^{-1} from the faster, 3-ps decay time. The experimental linewidth is, however, 13 cm^{-1}. The experimental linewidth is therefore broadened by inhomogeneities and/or by pure dephasing. It cannot be used as a measure of the vibrational-energy-relaxation dynamics.

What is the nature of the intermediate level? Physically, the three-state model is valid when state $|c\rangle$ is anharmonically coupled to the transition which is being probed; molecules in state $|c\rangle$ must undergo a substantial shift in the transition frequency, ω_{ba}. In this way, they do not contribute to the vibrationally resonant SFG signal, an assumption in the model. As shown above, substrate heating does not cause such shifts. State $|c\rangle$ must in fact be another vibrational mode of the molecule which is anharmonically coupled to the symmetric C-H stretching mode. The fast decay process must therefore be due to intramolecular energy relaxation, and not to energy transfer with the substrate.

The modes which are the most likely candidates for the transient intermediate are the C-H asymmetric stretching mode and/or the C-H bending modes. These modes are anharmonically coupled to the symmetric stretch (50–100-cm^{-1} shifts), as required.[5] Fast equilibration of the C-H stretching modes, followed by relaxation to the C-H bending modes, has been proposed to account for two-component decays observed in vibrational-energy-transfer studies of small molecules in liquids.[8] Alternatively, rapid relaxation might instead occur directly to the C-H bending modes, followed by slow bending-mode relaxation.

Vibrational damping at metal surfaces by excitation of electron-hole pairs has been proposed as an efficient energy-transfer mechanism.[1] Previous estimates based upon indirect vibrational-linewidth measurements in similar adsorbate/metal systems [CH_3O/Cu(100), CH_3C/Pt(111)] have assigned the symmetric C-H stretching-mode relaxation to electron-hole-pair damping.[2] We have already shown that the first relaxation step in the present case is intramolecular, in contradiction to these assignments. We can compare the slower second component, as well, to an estimate of the damping rate for C-H stretching or bending modes with transition dipoles of 0.05 D, at a distance of approximately 2.5 Å (the estimated separation of the C-H dipole from the free-electron edge).[9] The relaxation time is estimated to be 6 ns, 2 orders of magnitude longer than the observed slow decay component. One might postulate an enhanced relaxation rate due to vibrational coupling to oscillatory charge flow between the metal and the molecule,[2] but this coupling would almost certainly imply electronic structure changes sufficient to cause a vibrational frequency shift. Virtually none (4 cm^{-1} compared to the liquid) is presented here. We conclude that vibrational damping by coupling to excitation of electron-hole pairs or to charge flow in the silver surface is not important in any of the observed dynamics.

Direct energy transfer to the substrate by multiphonon relaxation is also inconsistent with the slow-component relaxation rate. Relaxation by multiphonon emission directly to the silver substrate (Debye frequency $\sim$145 cm^{-1}) would require an improbable 10–20 phonon decay process and would have a much stronger temperature dependence than that shown in Fig. 3.[10] We assign the slow decay component instead to a second intramolecular relaxation step, based on its rate and its temperature dependence. The decay time is within a factor of 3 of the 165-ps decay time observed for relaxation of the symmetric CH_3 stretching mode in Langmuir-Blodgett monolayers, where intramolecular relaxation dominates.[3] The temperature dependence is consistent with a relaxation process in which the excited level couples to two or three lower-frequency modes of the molecule. For instance, the solid line in Fig. 3 is obtained from a perturbative expression for the multiphonon decay rate[10] assuming that the C-H stretching mode (2920 cm^{-1}) couples to an overtone of the C-H deformation (two modes at 1360 cm^{-1}) with the excess energy exciting a low-frequency mode at 200 cm^{-1} (e.g., surface-substrate bond). This assignment is not unique, and two frequency experiments to directly probe the intermediate modes are needed to confirm specific relaxation pathways.

In summary, we report measurements of the relaxation time of an adsorbate vibration of a well-characterized methyl thiolate monolayer on a Ag(111) surface, using transient SFG spectroscopy. Two-component relaxation times are observed, and are assigned to intramolecular vibrational relaxation. Substrate heating and coherent transitions do not interfere substantially with the energy-relaxation measurements. Direct coupling to the substrate through electron-hole-pair excitation or multiphonon emission is not consistent with the observed dynamics. This result indicates that previous assignments of the vibrational-relaxation mechanism to electron-hole-pair damping, based on indirect line-shape measurements of the symmetric stretching mode in similar adsorbates on metal surfaces,[2] must be reconsidered. These conclusions do not, of course, rule out an important role for electron-hole-pair damping in other systems, particularly for diatomic adsorbates with strong transition dipoles. We believe that time-domain experiments of the type described here will be a general tool to understand adsorbate vibrational relaxation in a wide variety of systems.

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